Ionically Conducting Gel Polymers Electrolytes

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During this period the activities have been focused on the preparation and the characterization of the first set of polymeric electrolyte samples to be sent to the U.S. ARL, Ft. Monmouth, NJ.

This set is constituted by an adequate quantity of samples with the following molar composition:

1) PAN 16/ PC 23/ EC 56.5/ $LiClO_4$ 4.5
2) PAN 16/ PC 23/ EC 56.5/ $LiAsF_6$ 4.5
3) PAN 16/ PC 23/ EC 56.5/ Li-Imide 4.5

These samples have been prepared following the preparative route described later in the text and characterized by determining ionic conductivities, cationic transference numbers and the electrochemical stability windows.

All the preparation procedures of the gel electrolytes and the related electrochemical measurements were carried out in an Argon filled glove box whose atmosphere had a moisture content constantly lower than 5 ppm.

Synthesis of the gel electrolytes

The chemicals used in the preparations were adequately purified and dried. PAN (Aldrich, reagent grade; average molecular weight of 150.000), lithium perchlorate ($LiClO_4$, Fluka, high-purity grade) and

trifluoromethanesulphone imide ($LiN(CF_3SO_2$, 3M, high-purity grade) were dried, for at least 24 hours, under vacuum at 60, 110 and 80 °C, respectively. Alikely, the lithium hexafluoroarsenate ($LiAsF_6$, 3M product) was dried under vacuum for 24 hours at 80°C. Ethylene carbonate (PC, Fluka high-purity grade) was dried with type 4A molecular sieves for 48 hours and then distilled under vacuum. Karl-Fisher titrations for both EC and PC indicated water content of less than 18 ppm.

The film preparation procedure consisted of three consecutive steps. Initially, the selected lithium salt (LiX) was dissolved in a solution formed by mixing PC and EC in the correct molar ratio.

The second gelation step consisted in the addition of the PAN powder to the PC/EC-LiX solution followed by the room temperature mixing of the slurry in order to ensure a good wetting of the PAN and its initial swelling. This step was completed by placing the pre-swelled mixture in a heated silicon oil bath at 100°C and by stirring until a clear viscous gel was formed. In the third final step the films were fabricated by casting the hot gels between spacers-furnished glass plates which allowed the samples thickness control.

Upon cooling at room temperature free-standing elastomeric films were formed.

Samples characterization

The characterization of the samples has consisted in determining the following three main electrochemical properties relevant to their exploitation in the field of Lithium batteries, namely:
- the ionic electrical conductivity;
- the cationic transference number;
- the electrochemical stability window.

Electrical conductivities were determined from AC impedance measurements utilizing a Solartron Mod. 1260 Frequency Response Analyzer with a SS/Gel/SS cell configuration (SS= Stainless Steel).

Lithium ion transference numbers were measured utilizing both the impedance method described by Bruce and Vincent[1] and the so-called 'time of fly' method described by Watanabe and co-workers[2].

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[1] P.A. Bruce and Vincent - J.Electroanal.Chem. 225 (1987),1.

[2] M.Watanabe, K.Sanui et al. - J.Appl.Phys. 57,1(1985),123

The anodic decomposition potentials were determined by the use of a three-electrode cell with lithium as both counter and reference electrodes.

Results and Discussion

Introduction. As is shown in the Figure 1 all samples showed a plastic-like physical consistency with films having , in some cases, slightly wet surfaces due to the fact that not all the solvent (PC and EC mixture) is interacting directly with the polymer chains[3].

The degree of transparency of the membranes depended on the nature of the lithium salt used: with the most transparent films in the case of $LiClO_4$ and the most opaque, with a light-yellow coloration, for the imide salt.

Electrical conductivity. For of all the prepared samples the conductivity showed a liquid-like behavior with very high values, ranging from about $8 \cdot 10^{-4}$ S/cm at 12.5°C to $8 \cdot 10^{-3}$ S/cm at 90°C (Fig.2). The electrical conductivity data are shown in the Arrhenius plots of Fig. 2. Throughout the entire temperature range of the measurements (285 - 363 K), the Arrhenius plots exhibit significant curvature, which is characteristic of Vogel-Tamman-Fulcher (VTF) behavior. The ionic conductivities of the three samples are quite high even below the room temperature, having values of about 10^{-3} S/cm at 12.5°C. By a regression analysis of the conductivity data on the VTF equation:

$$\sigma = A \cdot T^{1/2} \exp[-Ea / (T - To]$$

performed by the use of a non-linear least square best fitting program, it has been possible to obtain the To, A and Ea as fit-adjustable parameters.
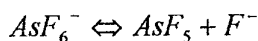
The three gels exhibited very similar values of Ea although the $EC/PC:LiClO_4$ sample is characterized by a somewhat low preexponential factor.

Anodic decomposition. Figure 3 shows the current voltage responses obtained for the three samples at room temperature. The trend of these

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[3] A.Tager - Physical Chemistry of Polymers, MIR Publishers, Moscow, 1978.

curves suggests that the gel electrolyte containing LiClO$_4$ is the most stable with the onset of the decomposition current reaching 5.0 V (curve a). A good satisfactory stability, up to 4.6 V, is also shown by the sample containing the Imide salt as electrolyte (curve c). Interesting is to note that the anodic curve in this case shows a current peak at 4.1 V (curve c). The nature of this peak is not yet understood. Some additional voltammetric data (not reported here) seem to suggest a partially reversible dissociation of the (N(CF$_3$SO$_2$)$_2$)$^-$ anion as the cause of the phenomenon.

The gel sample containing the LiASF$_6$ electrolyte shows the lowest value of the anodic decomposition potential (curve b and Table 1). This peculiar behavior is probably associable to the PAN decomposition catalyzed by the dissociation products of the (AsF$_6$)$^-$ according to the acid-base equilibrium[4]:

$$AsF_6^- \Leftrightarrow AsF_5 + F^-$$

Li$^+$ Transference Numbers. Table 1 shows the Li$^+$ transference number values of the three samples obtained by the two different techniques previously cited in the 'samples characterization' section.

Generally, the $t_{Li}+$ values obtained by the 'time of fly' method are lower than those obtained by the Bruce and Vincent's one. Furthermore, the values of the transference numbers we have measured for the PAN-gel electrolytes (Table 1) are much higher than those usually reported for liquid and PEO-based polymer electrolytes. Although an high value of $t_{Li}+$ is a beneficial characteristic for gel electrolytes to be exploited in solid-state polymeric electrochemical devices, one has to be aware that the techniques used for the $t_{Li}+$ determination may be associated to a certain degree of uncertainty, specially in high concentrated solutions where the extent of ion-ion and ion-solvent association is unpredictable. Nevertheless, taking into account the qualitative character of the data relative to $t_{Li}+$ in Table 1, it is worth to note that the sequence of the values is logical since they increase in the same order of the increases of the size of the anions, namely (ClO$_4$)$^-$ > (AsF$_6$)$^-$ > (N(CF$_3$SO$_2$)$_2$)$^-$.

Future Works

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[4] G. Dautzenberg, F.Croce, S. Passerini, B. Scrosati - Chem. Mater. 1994, 6, 538-542

In this study it has been demonstrated that gel electrolytes based on PAN have the prerequisites for their exploitation as electrolytic membranes in practical electrochemical devices. In particular the high ionic conductivities, very close to that of liquid electrolyte solutions based on aprotic lactones, the elevated electrochemical stability windows and the satisfactory Li^+ transference numbers confer to these membranes the suitability for their use in the realization of lithium-based high energy density rechargeable batteries. Nevertheless, the PAN-based gel electrolytes have shown a not complete retention of the gelating solvents[3] as the result of a not complete interaction between the polymeric chains and the solvent molecules. Due to this phenomena the surfaces of the films are, unavoidably, wetted and some solvent is able to freely react with the lithium anode of the batteries.

In order to try to avoid or reduce this undesired phenomena we have started the preparation and the characterization of a new class of gel electrolytes based on (poly)methilmethacrylate(PMMA) polymeric matrix. Preliminary investigations show these latter electrolytes have a very high degree of solvent retention joined with a good conductivity. The complete characterization of these samples will be the object of the second interim report.

Figure captions

Figure 1: Picture of a tipical PAN-based electrolytic gel
film;

Figure 2: Arrhenius plots of the three gel samples;

Figure 3: Decomposition potentials at 20°C of the three
gel electrolytes. Scan rate: $1mVs^{-1}$.
$LiClO_4$-PC/EC-PAN (curve a)
$LiAsF_6$-PC/EC-PAN (curve b)
$Li(CF_3SO_2)_2$-PC/EC-PAN (curve c)

Table 1

Electrochemical properties of poly(acrylonitrile)-based gel electrolytes at 25°C.

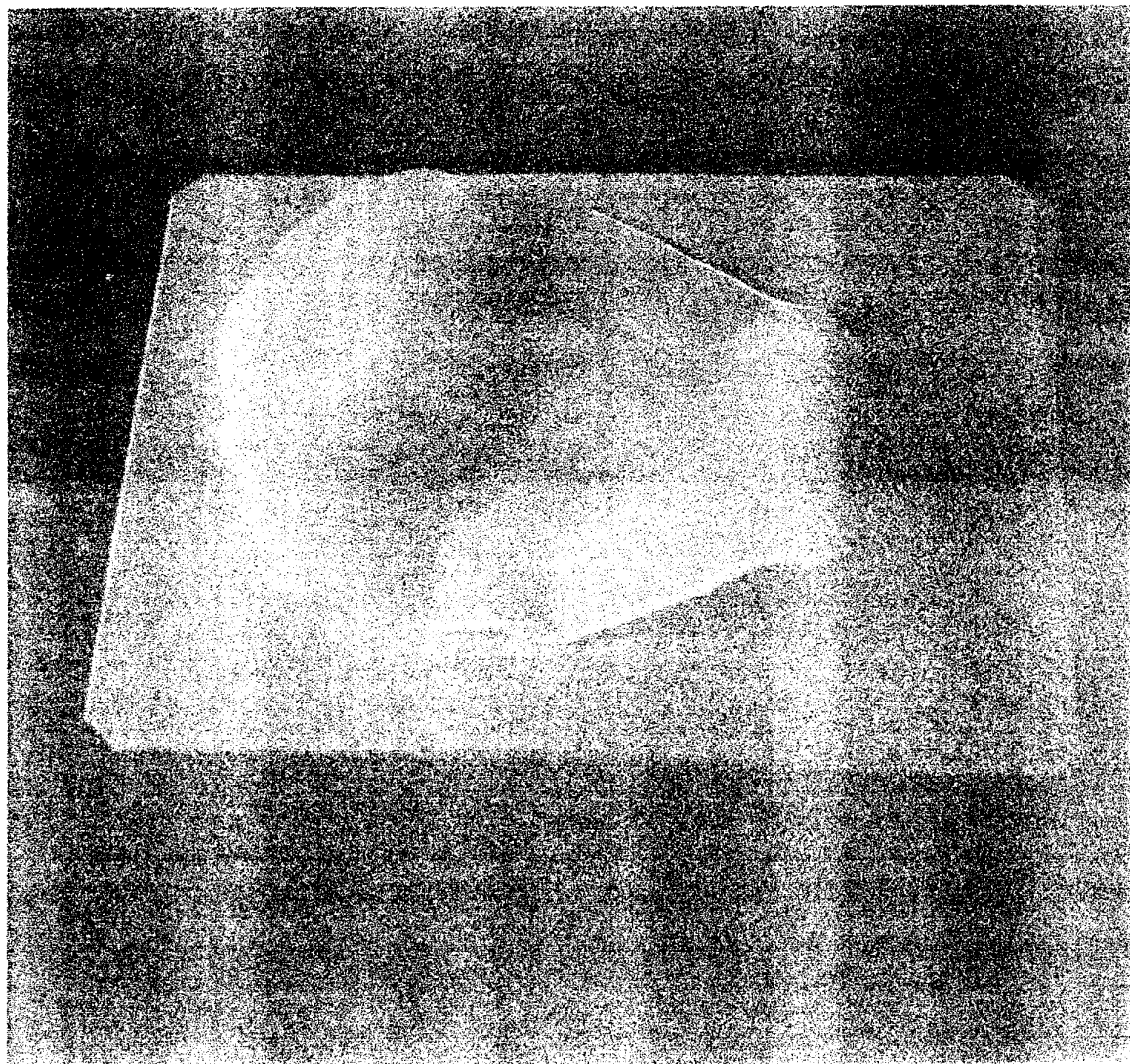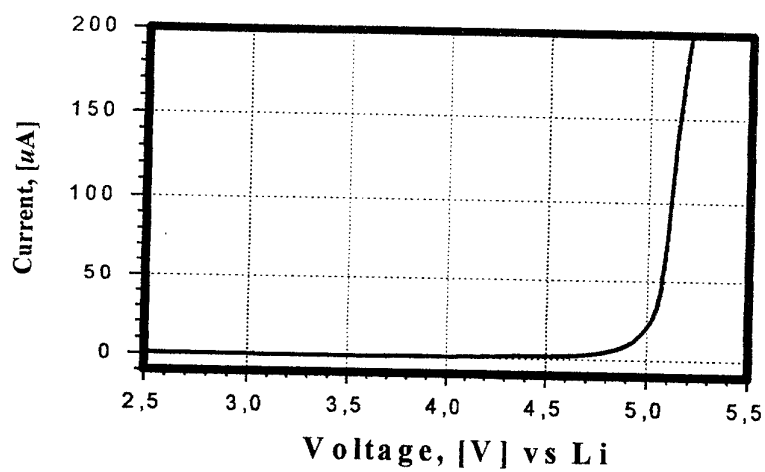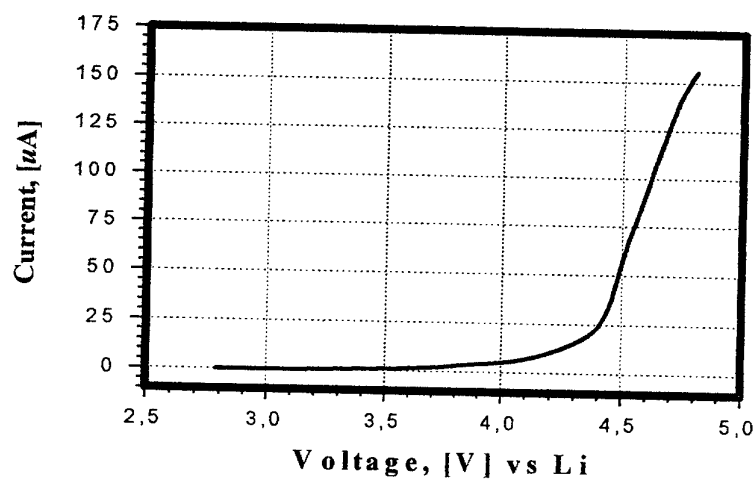| Electrolyte membrane	Conductivity [$Scm^{-1} \times 10^{-3}$]	Li^+ Transfer number	Anodic stability [V] vs Li
$LiClO_4$, PC:EC, PAN	1.1	0.5-0.6	5.0
$LiAsF_6$, PC:EC, PAN	0.9	0.6-0.7	4.3
$LiN(CF_3SO_2)_2$, PC:EC, PAN	1.0	0.7-0.8	4.6

Figure 2

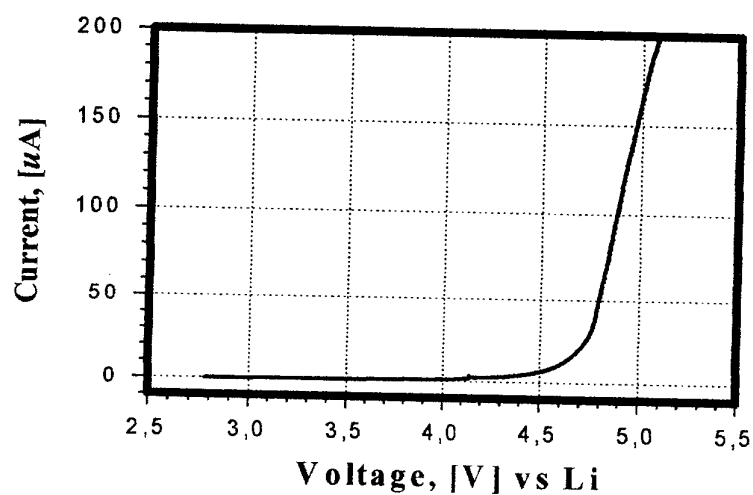## Arrhenius plot of poly(acrylonitrile)-based gel electrolytes.

Legend:
- LiClO$_4$, PC:EC, PAN
- LiAsF$_6$, PC:EC, PAN
- LiN(CF$_3$SO$_2$)$_2$, PC:EC, PAN

a

b

c

Figure 3